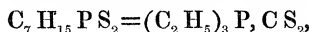


XIV. "Researches on the Phosphorus-Bases."—No. XIII.  
Sulphuretted Derivatives of Triethylphosphine. By A. W.  
HOFMANN, LL.D., F.R.S. Received May 24, 1861.

In the former Notes of my researches on the phosphorus-bases, I have repeatedly alluded to the beautiful red crystals,



which are formed by the action of disulphide of carbon on triethylphosphine. I have pointed out that the facility and rapidity with which they are formed, render disulphide of carbon a most valuable reagent for the phosphorus-bases (trimethylphosphine exhibiting a perfectly similar deportment), since neither the monarsines nor the monostibines are in any way affected by this substance.

On the other hand, triethylphosphine may be employed with the greatest advantage as a test for disulphide of carbon. There is, in fact, no test for this substance which in delicacy could be compared with triethylphosphine. By its aid the presence of the disulphide in the most volatile fractions of coal-tar-benzol is readily proved; even the exceedingly small quantity of disulphide of carbon diffused in the most carefully purified coal-gas, may, as I have shown already in another place\*, be recognized without any difficulty.

In describing in a previous Note the formation and composition of the disulphide-of-carbon-compound, I have already mentioned the peculiar transformation which this substance suffers under the influence of water, being converted under these circumstances into the sulphide of triethylphosphine.

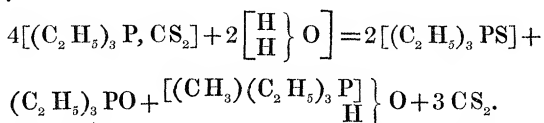
I have of late minutely examined this remarkable reaction.

The transformation is most conveniently studied by digesting the disulphide-of-carbon-compound with water in sealed tubes. After three or four days' exposure to 100°, the red crystals have disappeared, being replaced by the slender crystals of the sulphide. The latter compound is accompanied by several other products, the nature of which varies according to the duration of the reaction. In the first stages of the process considerable quantities of disulphide of carbon are separated, which in the latter stages may be traced in its products of decomposition, carbonic acid and sulphuretted hydrogen. The

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mother-liquor of the sulphide of triethylphosphine is distinctly alkaline, and yields, after the necessary operations, on addition of dichloride of platinum, the well-known octohedral platinum-salt of methyl-triethyl-phosphonium. On further evaporating the liquid from which these crystals had been obtained, the six-sided tables of the platinum-salt of oxide of triethylphosphine were deposited.

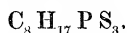
The principal products of the action of water upon the red crystals, then, are sulphide of triethylphosphine, oxide of triethylphosphine, hydrate of methyl-triethylphosphonium, and disulphide of carbon, which may be partly or entirely converted into sulphuretted hydrogen and carbonic acid. Four molecules of the disulphide of carbon-compound, and two molecules of water, contain the elements of two molecules of the sulphide, one molecule of the oxide, one molecule of the hydrated phosphonium, and three molecules of disulphide of carbon :—



Whilst engaged with the experiments involved in the elucidation of this subject, I observed occasionally small well-defined yellow crystals disseminated among the mixture of white and red needles, which were deposited when the digestion-tubes were allowed to cool before the transformation was terminated. The yellow crystals appeared in greater quantity towards the close of the operation, but were even under the most favourable circumstances obtained only in extremely minute quantity.

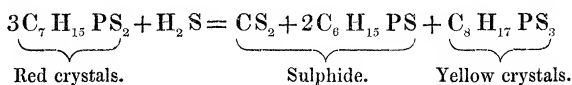
These crystals are almost insoluble in ether, and may therefore be readily separated from the sulphide of triethylphosphine with which they are contaminated. Crystallization from boiling absolute alcohol furnishes them in a state of perfect purity, occasioning, however, a certain loss, which may become very considerable if ebullition be continued for some time. This substance is decomposed at 100°, and had therefore to be dried for analysis, *in vacuo*, over sulphuric acid.

The yellow crystals were found to contain



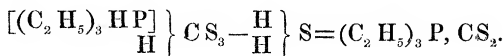
The formation of a compound of this formula by the action of water upon the red crystals is easily understood, if we recollect the

separation, during the principal phase of this process, of disulphide of carbon, and therefore, in consequence of a secondary reaction, of sulphuretted hydrogen which, more especially during the latter stages of the operation, is apt to accumulate to a very considerable extent in the liquid. Three molecules of the red disulphide-of-carbon-compound, and one molecule of sulphuretted hydrogen contain the elements of one molecule of disulphide of carbon, two molecules of sulphide of triethylphosphine and one molecule of the yellow crystals,

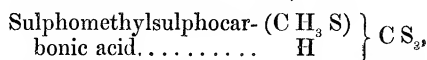
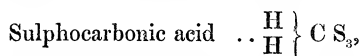


That the formation of the yellow crystals is actually due to the action of sulphuretted hydrogen is unequivocally proved by a synthetical experiment. The red disulphide-of-carbon-compound, when digested at  $100^\circ$  in sealed tubes with a saturated solution of sulphuretted hydrogen, is rapidly converted into the yellow crystals. I have thus succeeded in preparing considerable quantities of this substance, of which, as long as it was only obtained as a secondary, I might almost say accidental, product of the reaction, I had great difficulty in procuring a sufficient quantity for analysis.

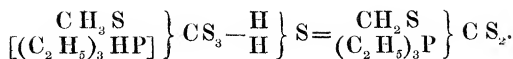
The constitution of the yellow crystals, like that of the red compound from which they originate, is rather obscure. I have already pointed out on a former occasion that the red compound may be viewed as the primary triethylphosphonium-salt of sulphocarbonic acid *minus* one molecule of sulphuretted hydrogen,



If we imagine a sulphocarbonic acid in which one equivalent of hydrogen is replaced by the monatomic radical  $\text{CH}_3\text{S}$  (methylene-mercaptam *minus* the molecular residue of sulphuretted hydrogen),



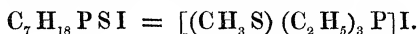
the yellow crystals may be viewed as the triethylphosphonium-salt of sulphomethylated sulphocarbonic acid *minus* one molecule of sulphuretted hydrogen,



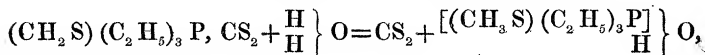
The view which I am taking of the constitution of the yellow crystals is supported by a remarkable transformation which this substance undergoes under the influence of boiling water.

I have already mentioned that this compound cannot be recrystallized from boiling alcohol without loss. The substance is likewise readily soluble in boiling water, but the solution contains no longer the original compound, and no crystals are deposited either on cooling or on evaporation. During ebullition the yellow compound is entirely destroyed, disulphide of carbon being abundantly evolved. The residuary liquid exhibits a faintly alkaline reaction, and yields with acids well crystallized saline compounds. The finest of these salts is the iodide which, being very soluble in boiling and only sparingly soluble in cold water, may easily be obtained in long well-formed needles of perfect purity.

Analysis has proved this substance to contain



This formula represents the iodide of a sulphomethyl-triethylphosphonium, the derivation of which from the yellow compound may be readily traced. One molecule of the latter and one molecule of water contain the elements of one molecule of disulphide of carbon and one molecule of hydrate of sulphomethyl-triethylphosphonium,



which, when treated with acids, yields the corresponding salts.

I have not been able to eliminate the hydrate again from the iodide. When treated with oxide of silver, this compound loses its iodine, but not without its sulphur being likewise attacked, the last traces of which are separated, however, only after protracted ebullition. Considerable quantities of triethylphosphine are evolved during ebullition, and the liquid filtered off from the black precipitate, consisting of sulphide and iodide of silver mixed with metallic silver, contains the hydrates of argento-triethylphosphonium and methyl-triethylphosphonium, together with the sulphates of these bases.